

Chemistry of Transition Metals

Part 1. General Considerations

Mg	3	4	5	6	7	8	9	10	11	12	Al
Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga
Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In
Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl
Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg		

- Filling of 3d, 4d, and 5d shells
- In s- and p-block, electrons added to outer shell.
- In d-block, electrons added to penultimate shell expanding it from 8-18
- Most elements have incompletely filled d-shell (interesting properties)

Transition elements

1. Metals
2. Almost all: HARD, STRONG, High m.p., b.p.
3. Conduct heat & electricity
4. Form Alloys
5. Show variable oxidation states
6. At least one of the ions & compounds colored.
7. Form paramagnetic species because of partially filled shells
8. Form coordination compounds (complexes) and organometallic compounds.

Variable oxidation state

Sc			+3				
Ti	+1	+2	+3	+4			
V	+1	+2	+3	+4	+5		
Cr	+1	+2	+3	+4	+5	+6	
Mn	+1	+2	+3	+4	+5	+6	+7
Fe	+1	+2	+3	+4	+5	+6	
Co	+1	+2	+3	+4	+5		
Ni	+1	+2	+3	+4			
Cu	+1	+2	+3				
Zn		+2					

1. Increase in the number of oxidation states from Sc to Mn. All possible states exhibited by only Mn.
2. Decrease in the number of oxidation states from Mn to Zn, due to the pairing of d-electrons occurs after Mn (Hund's rule).
3. Stability of higher oxidation states decreases along Sc to Zn. Mn(VII) and Fe(VI) are powerful oxidizers.
4. Down the group, the stability of high oxidation states increases (easier availability of both d and s electrons for ionization).

Transition metal oxidation states

Sc 3	Ti 3,4	V 2, 3, 4, 5	Cr 2, 3, 4, 6	Mn 2, 3, 4, 6, 7	Fe 2, 3	Co 2, 3	Ni 2	Cu 1, 2	Zn 2
Y 3	Zr 4	Nb 3,4, 5	Mo 2,3,4, 5, 6	Tc 2,3,4, 5,6,7	Ru 2,3,4, 5,6,7, 8	Rh 1, 3	Pd 2, 4	Ag 1	Cd 2
La 3	Hf 4	Ta 3, 4, 5	W 2,3,4, 5, 6	Re 2,3,4, 5,6,7	Os 3,4,5, 6,7,8	Ir 1, 3	Pt 2, 4	Au 1, 3	Hg 1, 2

These are “common” oxidation states. It is not supposed to be an exhaustive list.

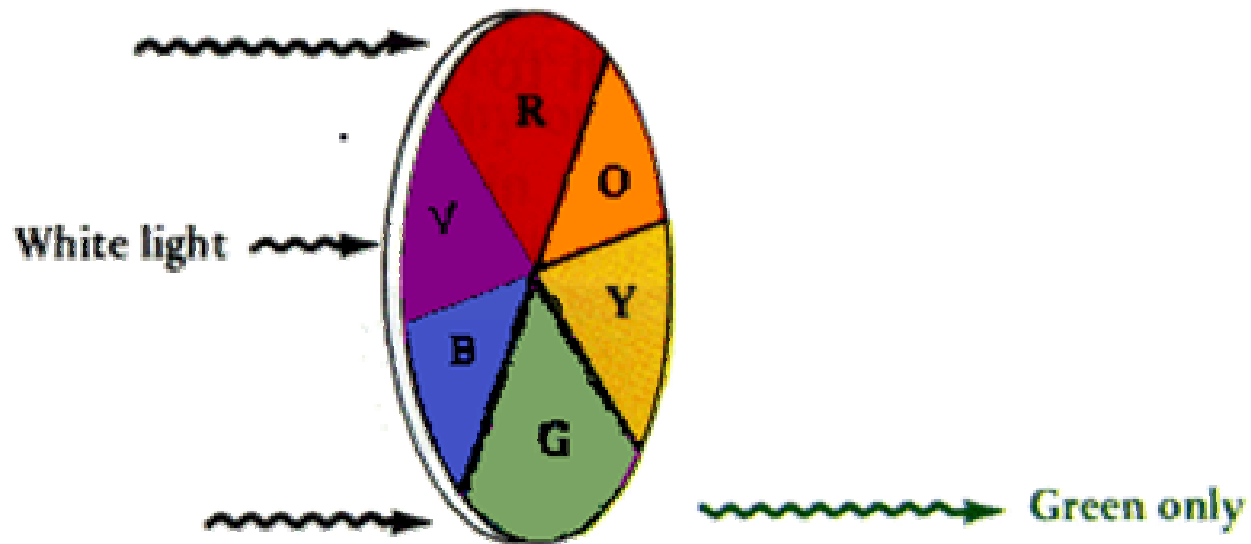
Low oxidation states of heavy metals like Ta, Nb, Mo, W and Re tend to be found in compounds containing metal-metal bonds

Color

- 1. The d-orbitals of the metal interact with the electron cloud of the ligands in such a manner that the d-orbitals become non-degenerate. When the d-level is not completely filled, it is possible to promote an electron from a lower energy d-orbital to a higher energy d-orbital by absorption of a photon of electromagnetic radiation having an appropriate energy (*d-d transitions*).**
- 2. *Metal to Ligand and Ligand to Metal Charge Transfer (LMCT and MLCT) transitions (KMnO₄)***
- 3. Electromagnetic radiations in the visible region of the spectrum often possess the appropriate energy for the above transitions.**

Color

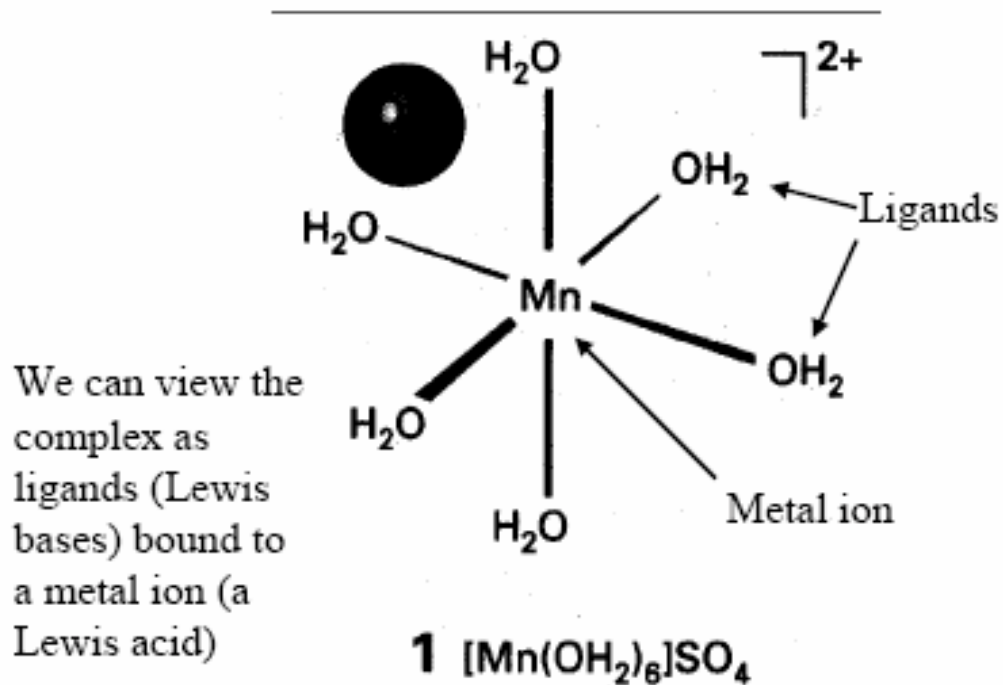
(a) Sample absorbs all but green light. Green is perceived.



Transition metal complexes

- ◆ A transition metal complex is species consisting of a transition metal coordinated (bonded to) one or more ligands (neutral or anionic non-metal species)
- ◆ Transition metal complexes are important in catalysis, materials synthesis, photochemistry, and biological systems
- ◆ Display diverse chemical, optical and magnetic properties

An example of a complex



Coordination numbers

- ◆ Transition metal ions usually form complexes with a well defined number of ligands
- ◆ Complexes with coordination numbers four and six are the most common, although two and five coordination are also very well established
- ◆ Coordination number and geometry are determined by a combination of:
 - Metal ion size
 - Ligand size
 - Electronic factors (electron configuration, ligand type)

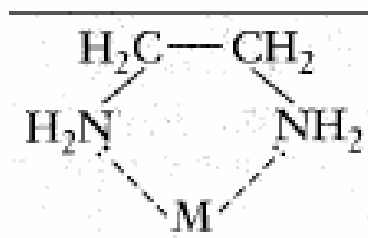
Ligands

- ◆ Ligands are species (neutral or anionic) bonded to the metal ion
- ◆ They may be attached to the metal through a single atom (monodentate) or bound to the metal through two or more atoms (bidentate, tridentate etc.)
- ◆ Polydentate ligands are called chelating ligands

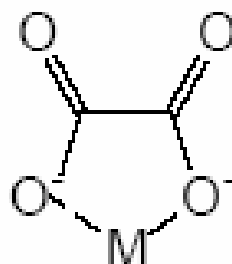
Example simple ligands

Neutral Molecules		Anions	
Aqua	H ₂ O	Fluoro	F ⁻
Ammine	NH ₃	Chloro	Cl ⁻
Methylamine	CH ₃ NH ₂	Bromo	Br ⁻
Carbonyl	CO	Iodo	I ⁻
Nitrosyl	NO	Hydroxo	OH ⁻
		Cyano	CN ⁻

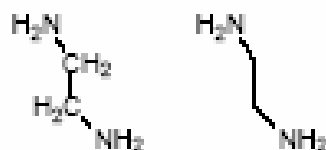
Example chelating ligands



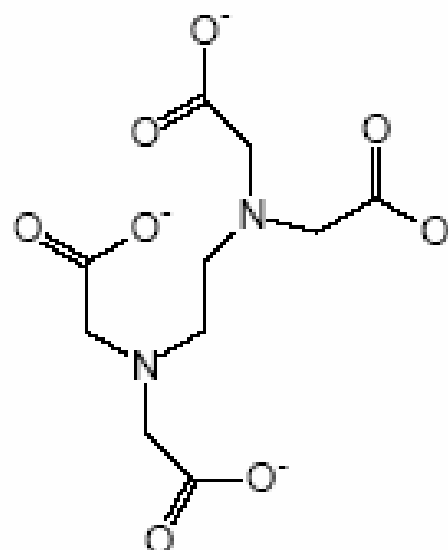
Ethylenediamine
acting as a bidentate
ligand



Oxalate acting
as a bidentate
ligand



Note both of these drawing
imply the same thing



Ethylenediaminetetraacetate
Can act as hexadentate ligand

Ligands and oxidation state

- ◆ Low oxidation state complexes can be stabilized by using ligands such as cyanide and carbon monoxide (π acceptor ligands – see later for explanation)
- ◆ Intermediate oxidation state complexes often have ligands such as chloride, ammonia or water
- ◆ High oxidation state complexes usually have fluoride or oxide as ligands

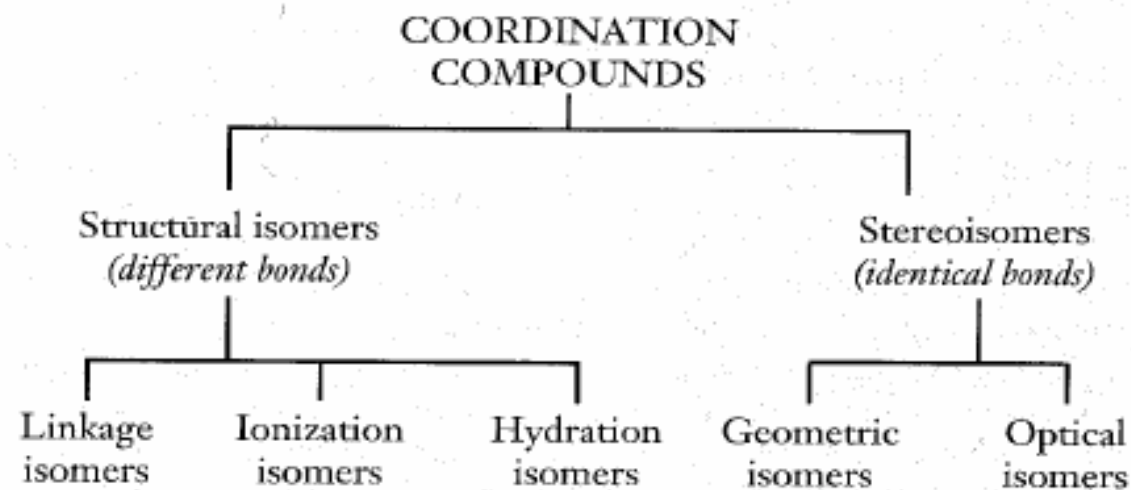
Self Study

Isomerism

Naming of complexes

Isomerism in metal complexes

- ♦ Isomers are compounds with the same chemical formula but different structures
 - Note that as they have different structures they will have different physical and chemical properties



Self Study

Naming of complexes

- ◆ The naming of compounds containing coordination complexes follows a set of well defined rules
 - 1) In a salt, the cation is always named before the anion
 - 2) The names of ligands are given in alphabetical order
 - > The names of coordinated anions end “o”, e.g. chloro, cyano etc.
 - > The names of neutral ligands are just the name of ligand molecule
 - > Some ligands have special names when they are in complexes eg. H_2O – aquo, NH_3 – ammine
 - 3) The number of ligands that present is indicated by a prefix, di, tri etc. However, if these prefixes are already in the name of the ligand bis, tris, tetrakis *etc.* are used instead
 - > Dichloro means two chloride ligands
 - > Bisethylenediamine means two ethylenediamine ligands
 - 4) After the ligands we specify the metal and its oxidation state as a roman numeral in brackets
 - > Platinum(II) indicates that we have platinum in an oxidation state of two

Part 2. Theories / Concepts

Bonding in transition metal compounds

- Werner Coordination Theory
- 18 electron rule
- Valence Bond Theory
- Crystal field theory
- Molecular orbital approach

High spin and low spin complexes

Spectrochemical series

CFSE

Jahn-Teller distortions

Werner Coordination Theory

Werner : 1893 (electron was discovered in 1896)

Nobel prize in 1913.

In complexes, metal ions show two different types of valency:

Primary Valency: Non-directional, is the number of charges on the complex ion.

1. Secondary Valency: Directional, equals to the number of ligands coordinated to the metal.

18 electron rule

(based on earlier EAN Rule: Sidgwick)

Stable low oxidation state complexes are found to have a total of 18 bonding electrons

metal electrons + lone pairs from ligands = 18

Ni(CO)₄ - 4s²3d⁸ and 4 lone pairs

Fe(CO)₅ - 4s²3d⁶ and 5 lone pairs

Cr(CO)₆ - 4s²3d⁴ and 6 lone pairs

The stability of these 18 electron species can be explained using MO theory.

Corresponds to filling all the molecular bonding orbitals and none of the antibonding orbitals

However, this rule only works for species with metals in a low oxidation state NOT FOR MOST COMPLEXES

Valence Bond Theory

- The idea that atoms form covalent bonds by sharing pairs of electrons was first proposed by G. N. Lewis in 1902.
- In 1927, Walter Heitler and Fritz London showed how the sharing of pairs of electrons holds a covalent molecule together. The Heitler-London model of covalent bonds was the basis of the VBT.
- The last major step in the evolution of this theory was the suggestion by Linus Pauling that atomic orbitals mix to form hybrid orbitals, such as the sp , sp^2 , sp^3 , dsp^3 , and d^2sp^3 orbitals.

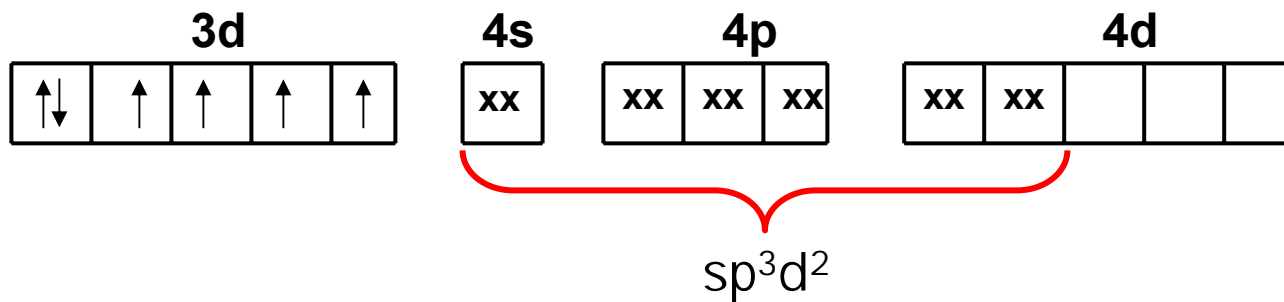
VBT – Assumptions / Features

- **Coordination compounds contain metal ions, in which ligands form covalent-coordinate bonds to the metal.**
- **Ligands must have a lone pair of electrons.**
- **Metal should have an empty orbital of suitable energy available for bonding.**
- **Atomic orbitals are used for bonding (rather than molecular orbitals)**
- **This theory is useful to predict the shape and stability of the metal complexes.**
- **Limitations: (1) Does not explain why some complexes are colored and others are not; (2) Does not explain the temp. dependence of the magnetic properties.**

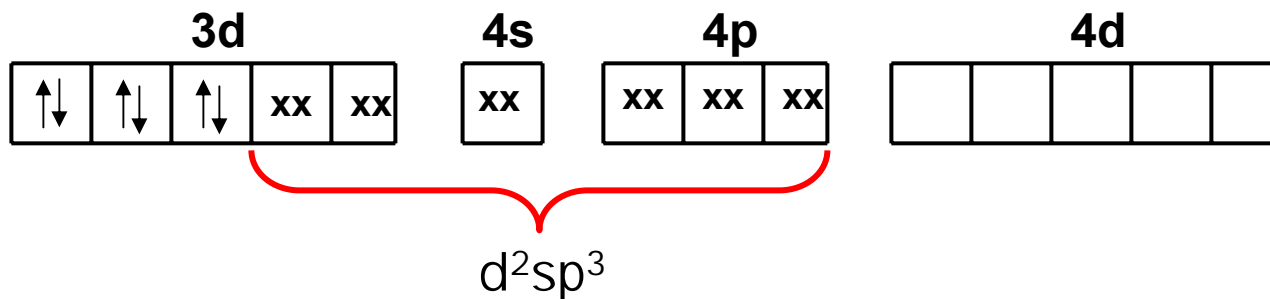
VBT - Example

➤ **Co: $3d^7 4s^2$**

➤ **$\text{Co}^{3+} : 3d^6 4s^0$**



Outer sphere complex
Reactive / labile
High spin
Paramagnetic



Inner sphere complex
Stable
Low spin
Diamagnetic

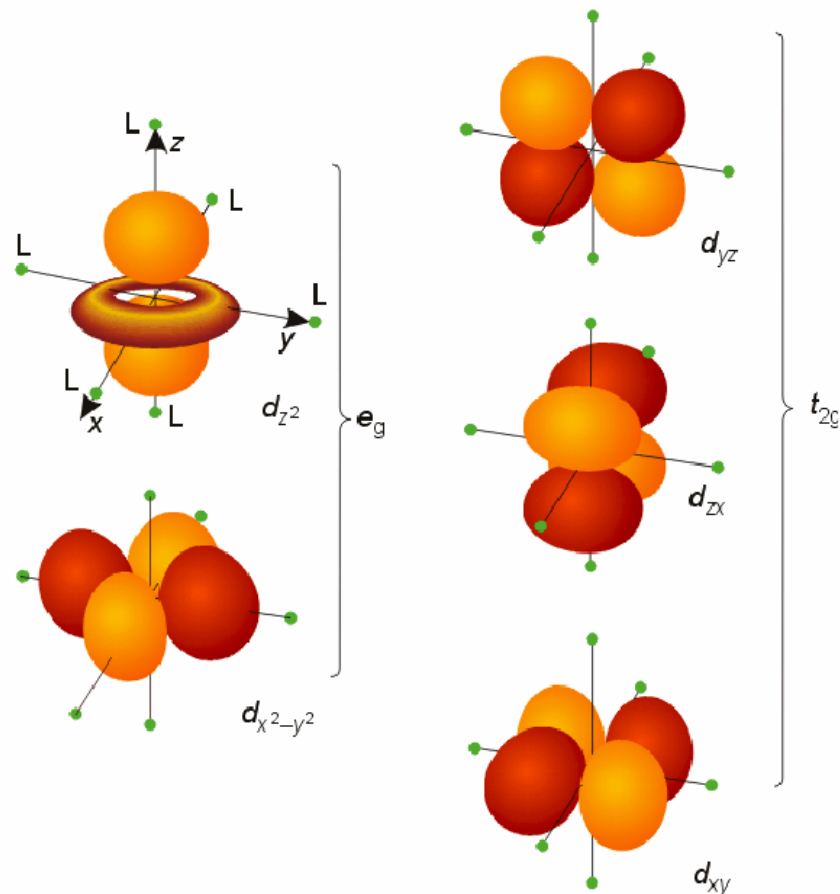
Crystal Field Theory

(Text : JD Lee; pp.204-222)

- This theory (**CFT**) largely replaced **VB Theory** for interpreting the chemistry of coordination compounds.
- It was proposed by the physicist Hans Bethe in 1929.
- Subsequent modifications were proposed by J. H. Van Vleck in 1935 to allow for some covalency in the interactions. These modifications are often referred to as **Ligand Field Theory**.
- For a review on the evolution of bonding models see:
C. J. Ballhausen, *J. Chem. Ed.* **1979** 56 194-197, 215-218, 357-361.

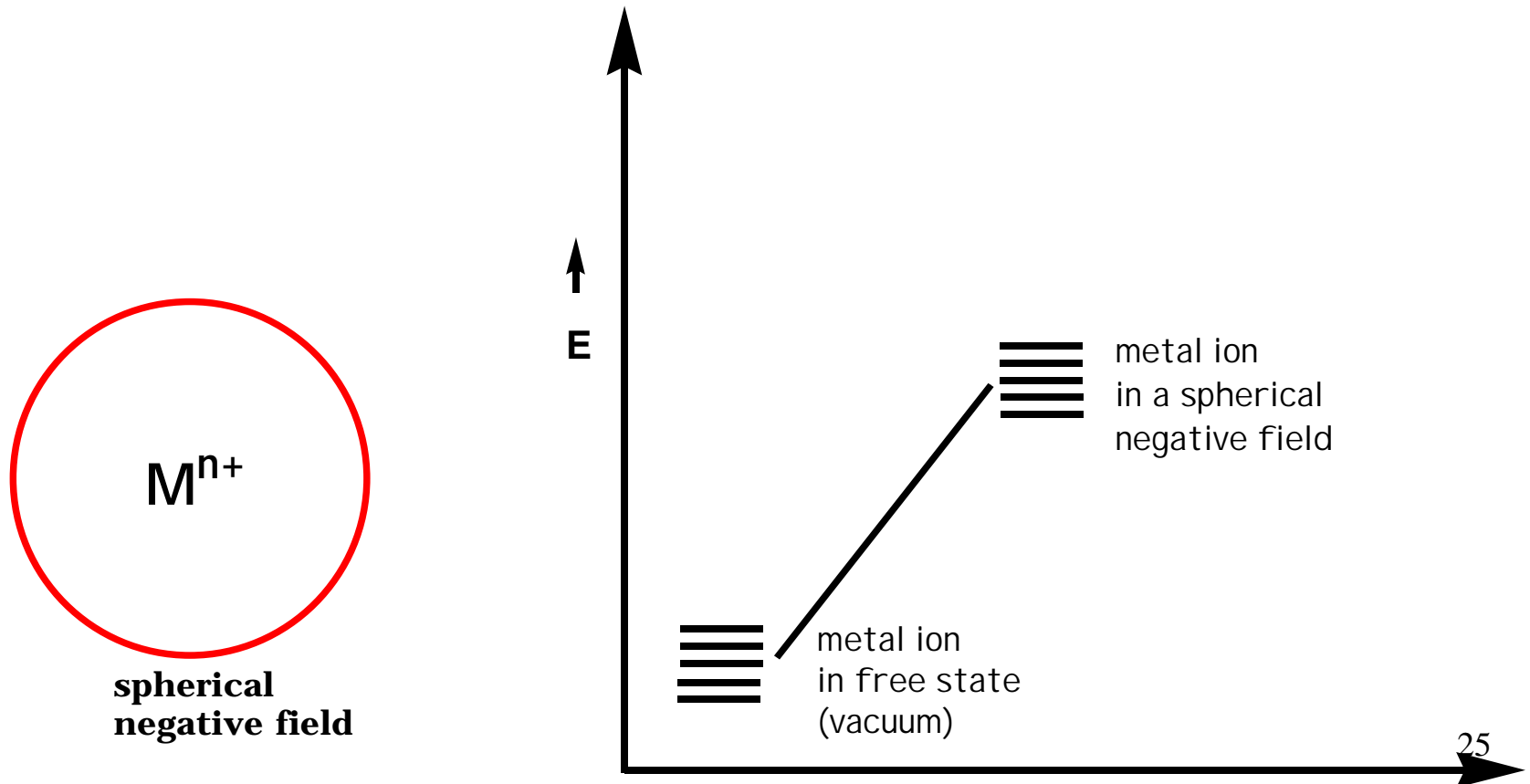
CFT – Assumptions

- The interactions between the metal ion and the ligands are purely electrostatic (ionic).
- The ligands are regarded as point charges
- If the ligand is negatively charged: ion-ion interaction. If the ligand is neutral : ion-dipole interaction
- The electrons on the metal are under repulsive from those on the ligands
- The electrons on metal occupy those d-orbitals farthest away from the direction of approach of ligands



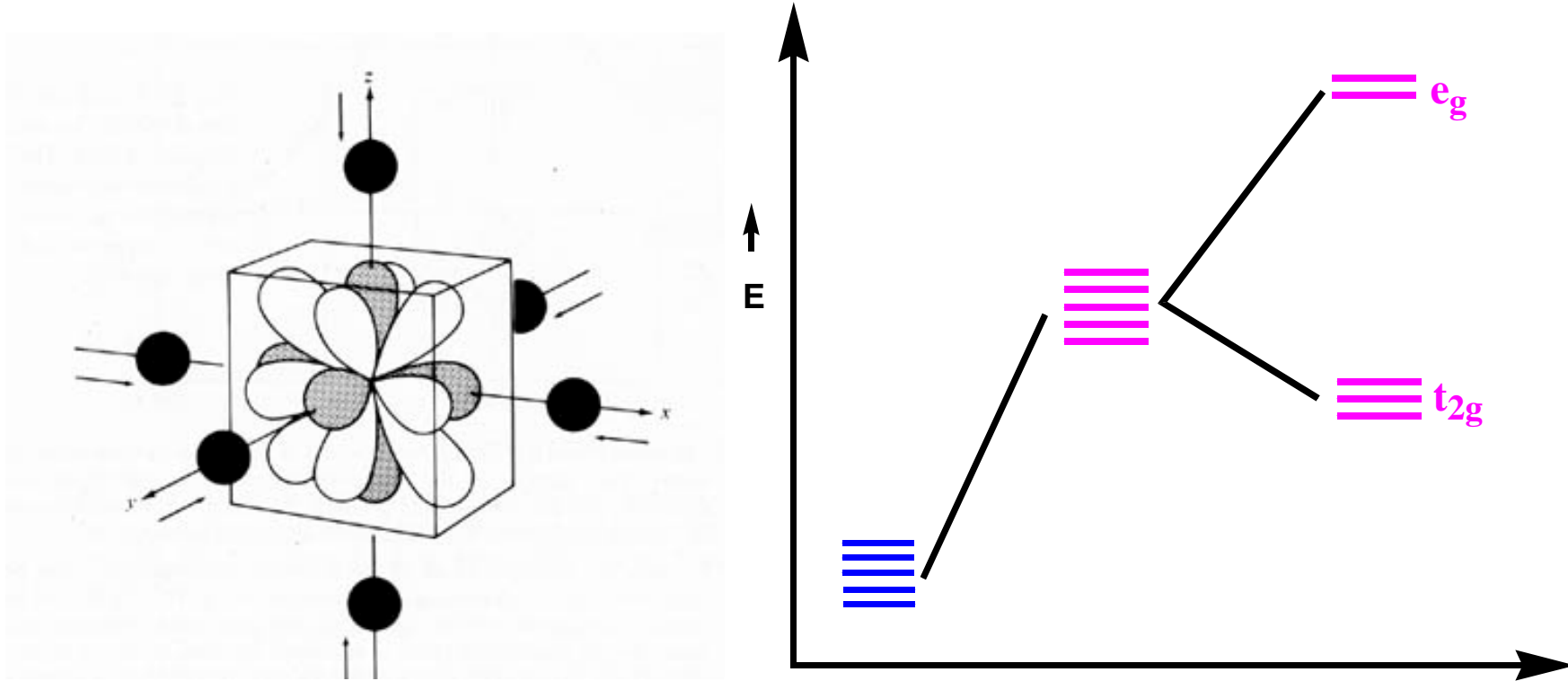
Symmetric Field

- The 5Xd orbitals in an isolated gaseous metal are degenerate.
- If a spherically symmetric field of negative charges is placed around the metal, these orbitals remain degenerate, but all of them are raised in energy as a result of the repulsion between the negative charges on the ligands and in the d orbitals.



Octahedral Field

• If rather than a spherical field, discrete point charges (ligands) are allowed to interact with the metal, the degeneracy of the d orbitals is removed (or, better said, lifted). The splitting of d orbital energies and its consequences are at the heart of crystal field theory.



• Not all d orbitals will interact to the same extent with the six point charges located on the $+x$, $-x$, $+y$, $-y$, $+z$ and $-z$ axes respectively.

• The orbitals which lie along these axes (i.e. x^2-y^2 , z^2) will be destabilized more than the orbitals which lie in-between the axes (i.e. xy , xz , yz).

Octahedral Complexes

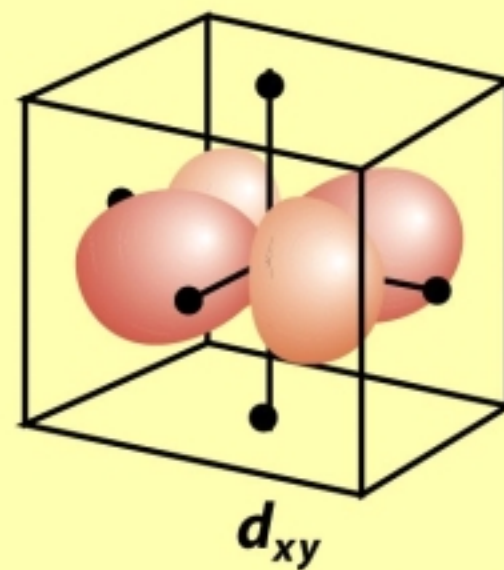
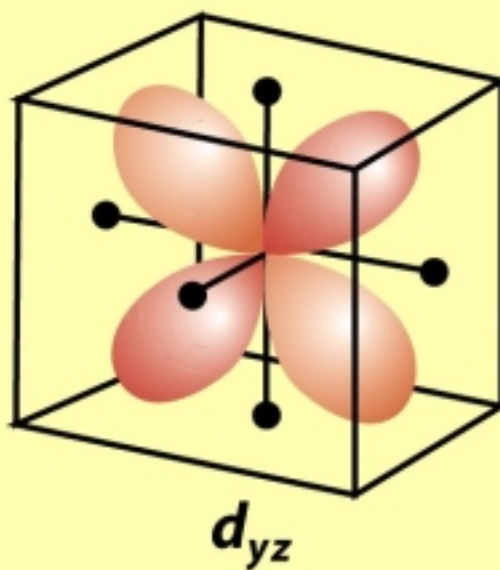
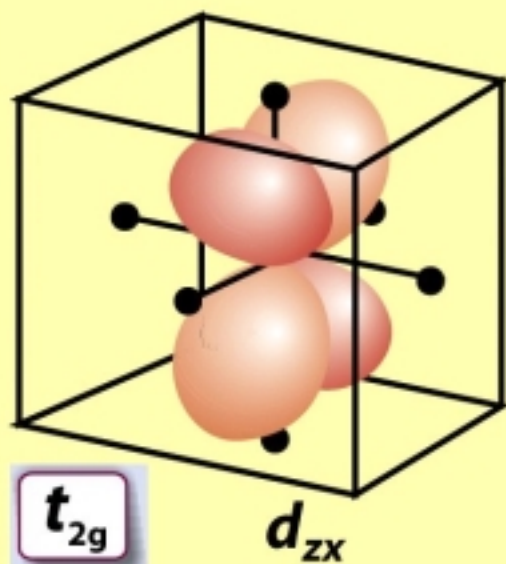
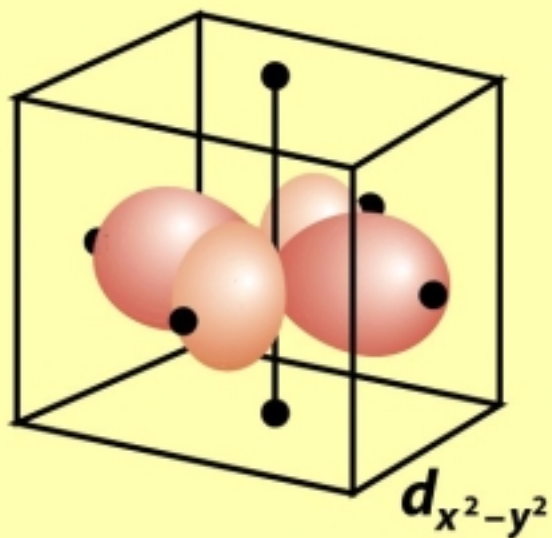
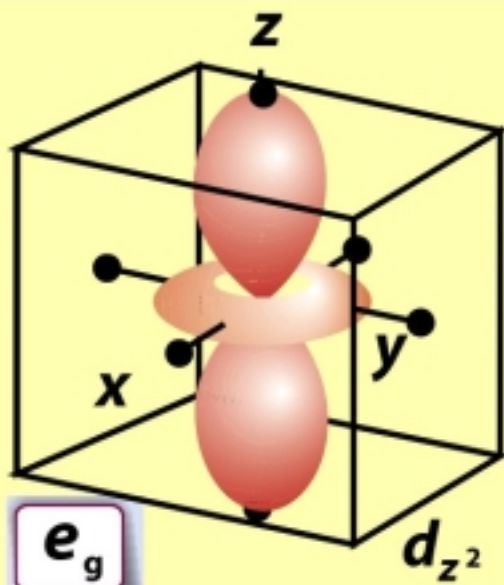


Figure 19-1
Shriver & Atkins Inorganic Chemistry, Fourth Edition
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CFT-Octahedral Complexes

- For the O_h point group, the x^2-y^2 , z^2 orbitals belong to the E_g irreducible representation and xy , xz , yz belong to the T_{2g} representation.
- The extent to which these two sets of orbitals are split is denoted by Δ_o or alternatively $10Dq$. As the **baricenter** must be conserved on going from a spherical field to an octahedral field, the t_{2g} set must be stabilized as much as the e_g set is destabilized.

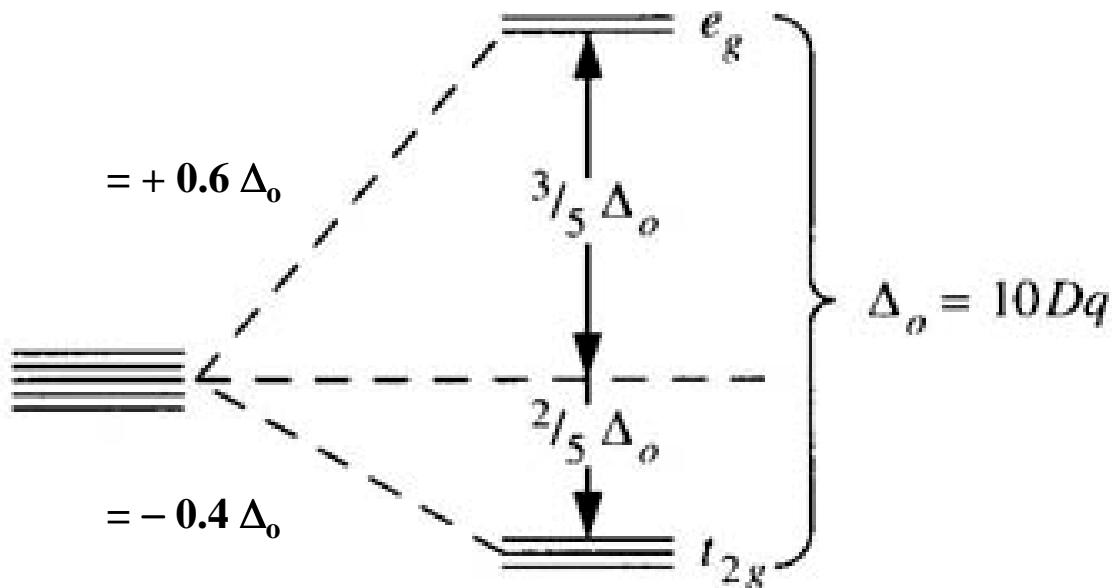
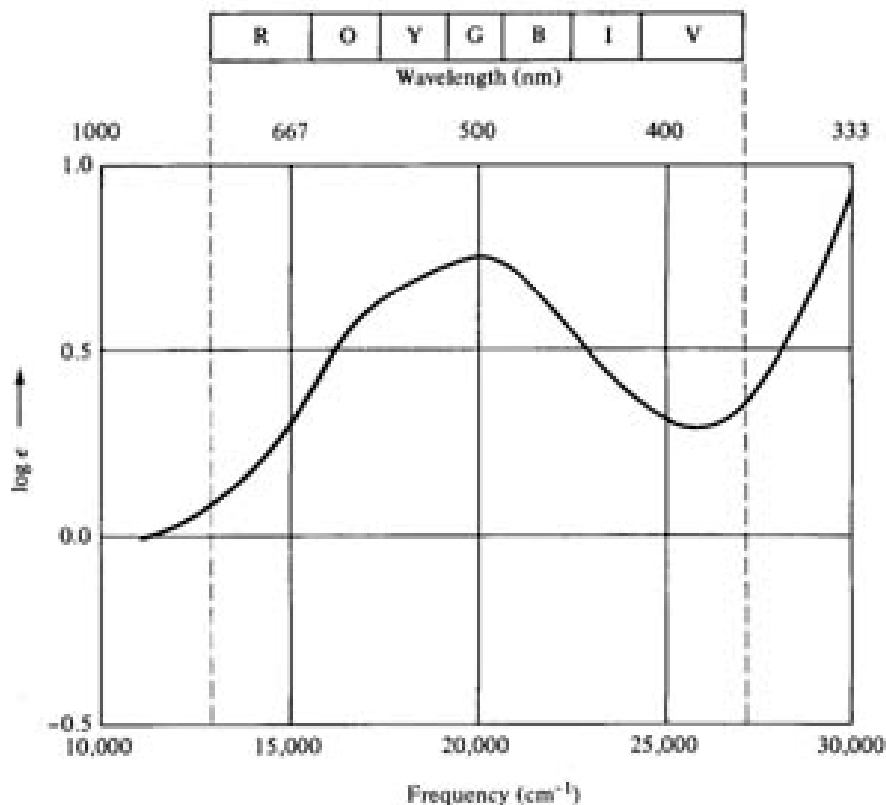


Illustration of CFSE

$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$: a d^1 complex and the e^- occupies the lowest energy orbital, i.e. one of the three degenerate t_{2g} orbitals. The **purple colour** is a result of the absorption of light which results in the promotion of this t_{2g} electron into the e_g level. $t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$



The UV-Vis absorption spectrum reveals that this transition occurs with a maximum at 20300 cm^{-1} which corresponds to Δ_o 243 kJ/mol.

($1000 \text{ cm}^{-1} = 11.96 \text{ kJ/mol}$ or
 2.86 kcal/mol or
 0.124 eV .)

Typical Δ_o values are of the same order of magnitude as the energy of a chemical bond.

- **What happens for more than 1 electron in d orbitals?**
- **The electron-electron interactions must be taken into account.**
- **For d^1 - d^3 systems:** Hund's rule predicts that the electrons will not pair and occupy the t_{2g} set.
- **For d^4 - d^7 systems** (there are two possibilities): Either put the electrons in the t_{2g} set and therefore pair the electrons (**low spin case** or **strong field situation**. Or put the electrons in the e_g set, which lies higher in energy, but the electrons do not pair (**high spin case** or **weak field situation**).
- Therefore, there are two important parameters to consider: **The Pairing energy (P), and the $e_g - t_{2g}$ Splitting (referred to as Δ_0 , $10Dq$)**
- For both the high spin (h.s.) and low spin (l.s.) situations, it is possible to compute the **CFSE**.

Δ_o vs Pairing Energy

Complex	Config.	Δ_o , cm ⁻¹	P, cm ⁻¹	spin-state
[Fe(OH ₂) ₆] ²⁺	d ⁶	10,400	17,600	high-spin
[Fe(CN) ₆] ⁴⁻	d ⁶	32,850	17,600	low-spin
[CoF ₆] ³⁻	d ⁷	13,000	21,000	high-spin
[Co(NH ₃) ₆] ³⁺	d ⁷	23,000	21,000	low-spin

Δ_o is dependent on:

- *Nature of the ligands*
- *The charge on the metal ion*
- *Whether the metal is a 3d, 4d, or 5d element*

Ligands which cause a small splitting are *Weak field ligands* (Δ_o in the range 7000 - 30000 cm^{-1}) and those cause a large splitting are *Strong field ligands* (CFSE typically > 30000 cm^{-1})

Spectrochemical Series

$\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^- < \text{Cl}^- < \text{N}_3^-$, $\text{F}^- < \text{urea}$, $\text{OH}^- < \text{ox}$, $\text{O}^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{py}$, $\text{NH}_3 < \text{en} < \text{bpy}$, $\text{phen} < \text{NO}_2^- < \text{CH}_3^-$, $\text{C}_6\text{H}_5^- < \text{CN}^- < \text{CO}$.

Δ_o is dependent on L:

$[\text{CrCl}_6]^{3-}$	13640 cm^{-1}	163 kJ/mol
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	17830	213
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	21680	314
$[\text{Cr}(\text{CN})_6]^{3-}$	26280	314

$[\text{Co}(\text{NH}_3)_6]^{3+}$	24800 cm^{-1}	163 kJ/mol
$[\text{Rh}(\text{NH}_3)_6]^{3+}$	34000	213
$[\text{Ir}(\text{NH}_3)_6]^{3+}$	41000	314

Table 19.1 Ligand-field splitting parameters Δ_o of ML_6 complexes*

Ions	Ligands					
		Cl^-	H_2O	NH_3	en	CN^-
d^3	Cr^{3+}	13 700	17 400	21 500	21 900	26 600
d^5	Mn^{2+}	7500	8500		10 100	30 000
	Fe^{3+}	11 000	14 300			(35 000)
d^6	Fe^{2+}		10 400			(32 800)
	Co^{3+}		(20 700)	(22 900)	(23 200)	(34 800)
	Rh^{3+}	(20 400)	(27 000)	(34 000)	(34 600)	(45 500)
d^8	Ni^{2+}	7500	8500	10 800	11 500	

* Values are in cm^{-1} ; entries in parentheses are for low-spin complexes.

Source: H.B. Gray, *Electrons and chemical bonding*. Benjamin, Menlo Park (1965).

Table 19-1

Shriver & Atkins Inorganic Chemistry, Fourth Edition

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For an octahedral complex, CFSE

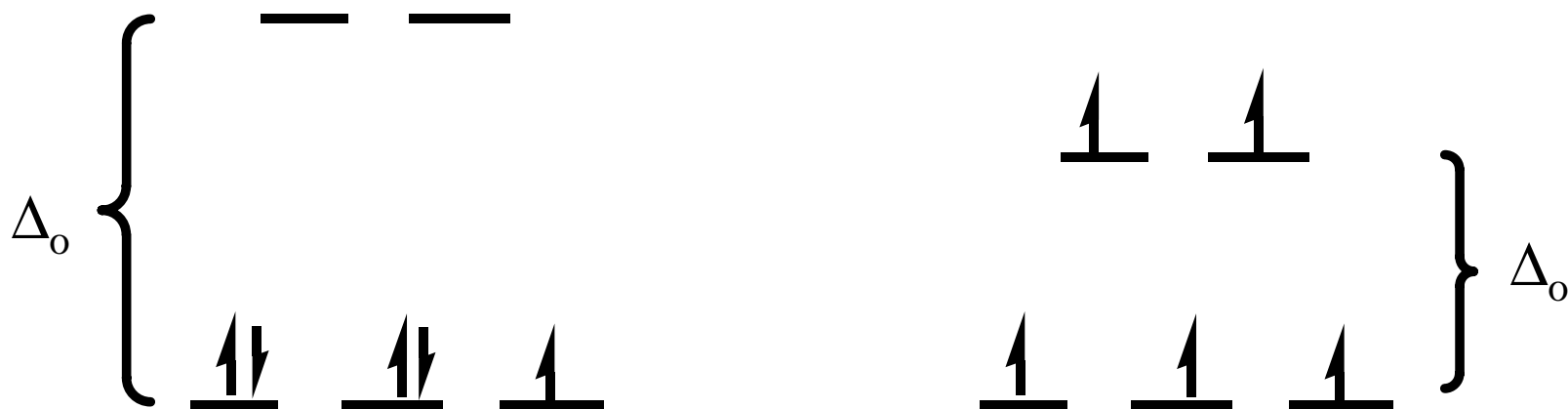
$$= -0.4 \times n(t_{2g}) + 0.6 \times n(e_g) \Delta_o$$

Where, $n(t_{2g})$ and $n(e_g)$ are the no. of electrons occupying the respective levels

If CFSE is very large, pairing occurs (i.e. $CFSE > P$)

If CFSE is rather small, no pairing occurs (i.e. $P > CFSE$)

d^5 system



Case I results in LS complex

Case II results in HS complex

Table 19.2 Ligand-field stabilization energies*

d^n	Example	Octahedral				Tetrahedral	
				N	LFSE	N	LFSE
d^0				0	0	0	0
d^1	Ti ³⁺			1	0.4	1	0.6
d^2	V ³⁺			2	0.8	2	1.2
d^3	Cr ³⁺ , V ²⁺			3	1.2	3	0.8
		Strong-field				Weak-field	
d^4	Cr ²⁺ , Mn ³⁺	2	1.6			4	0.4
d^5	Mn ²⁺ , Fe ³⁺	1	2.0			5	0
d^6	Fe ²⁺ , Co ³⁺	0	2.4			4	0.6
d^7	Co ²⁺	1	1.8			3	1.2
d^8	Ni ²⁺			2	1.2	2	0.8
d^9	Cu ²⁺			1	0.6	1	0.4
d^{10}	Cu ⁺ , Zn ²⁺			0	0	0	0

* N is the number of unpaired electrons; LFSE is in units of Δ_O for octahedra or Δ_T for tetrahedra; the calculated relation is $\Delta_T \approx 0.45\Delta_O$.

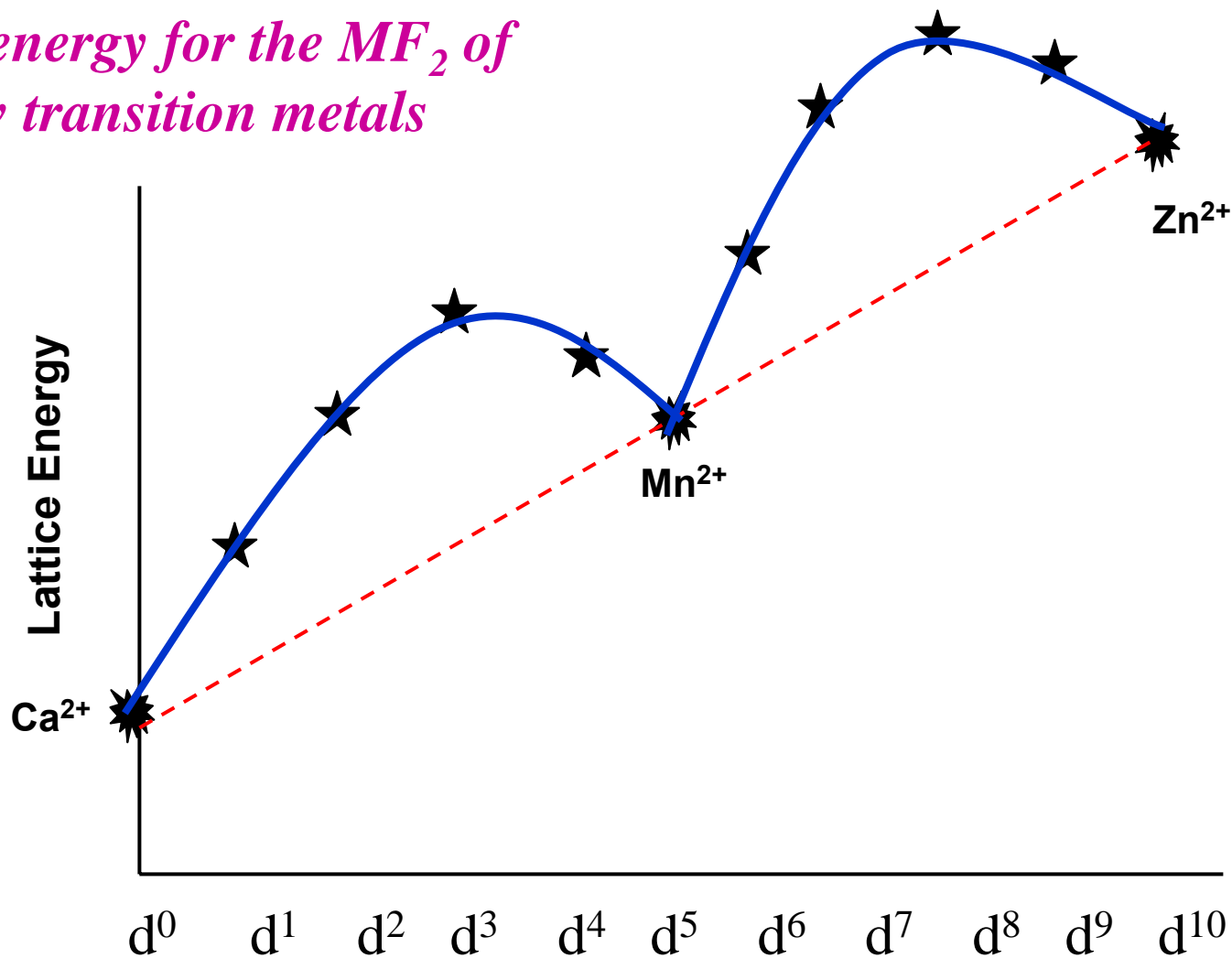
Table 19-2

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Applications of CFT

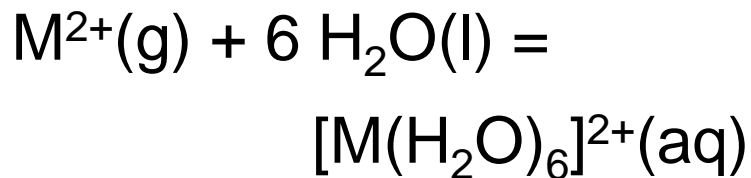
Lattice energy for the MF_2 of first row transition metals



F = weak field ligand

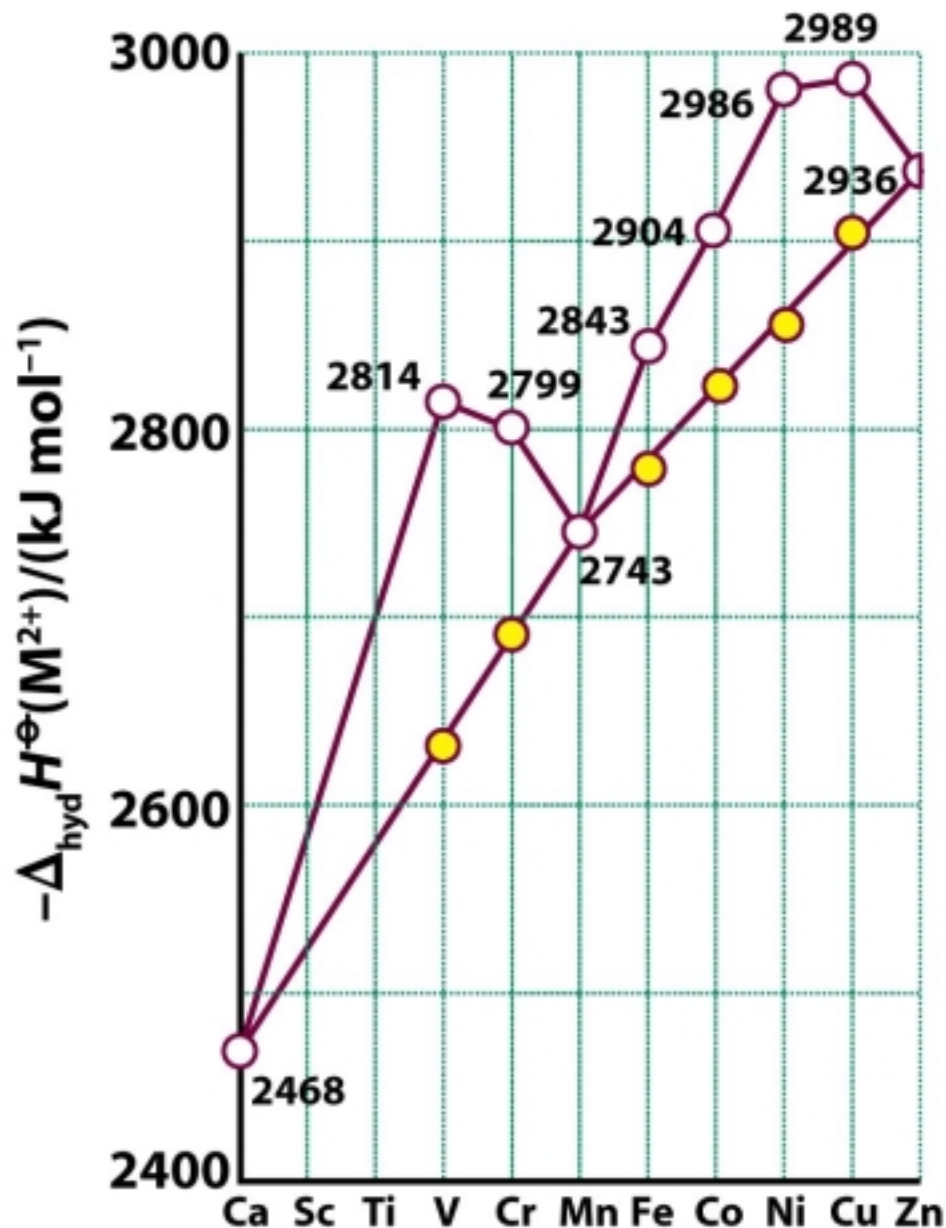
Applications of CFT

Hydration Enthalpy. Let us look at the variation of enthalpy of M^{2+} ions



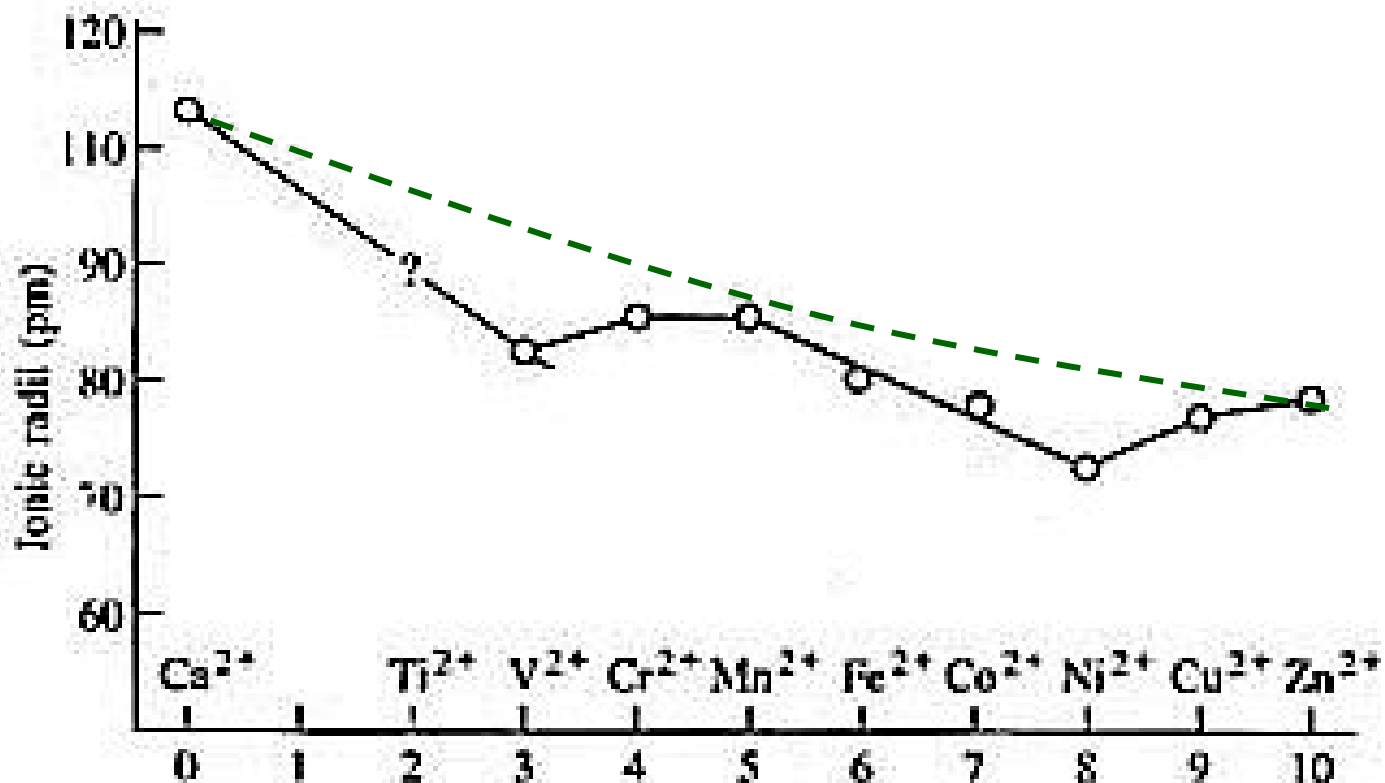
Ca^{2+} , Mn^{2+} , and Zn^{2+} have d^0 , d^5 , and d^{10} , hence CFSE is 0. Other metal ions deviate from the expected line due to extra CFSE

H_2O = weak field ligand



Applications of CFT

Ionic Radii. For a given oxidation state, the ionic radius decreases steadily on going from left to right in a transition series (dotted line).



Tetrahedral Field- Considerations

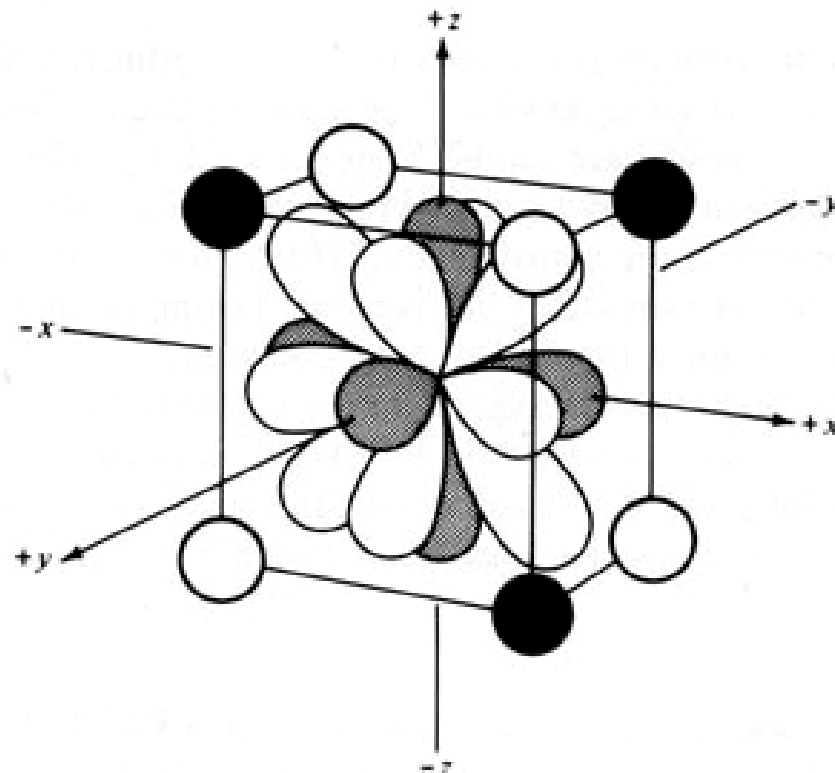
Imagine a tetrahedral molecule inside a cube with metal ions in the center of the cube. The ligands occupy the four alternate corners of the cube leaving the rest four corners empty.

The two 'e' orbitals point to the center of the face of the cube while the three 't₂' orbitals point to the center of the edges of the cube.

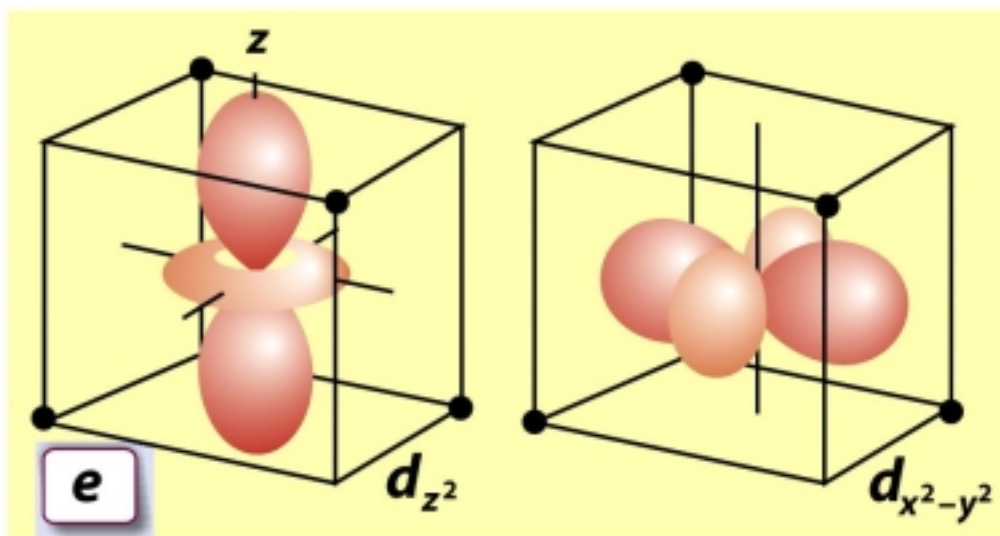
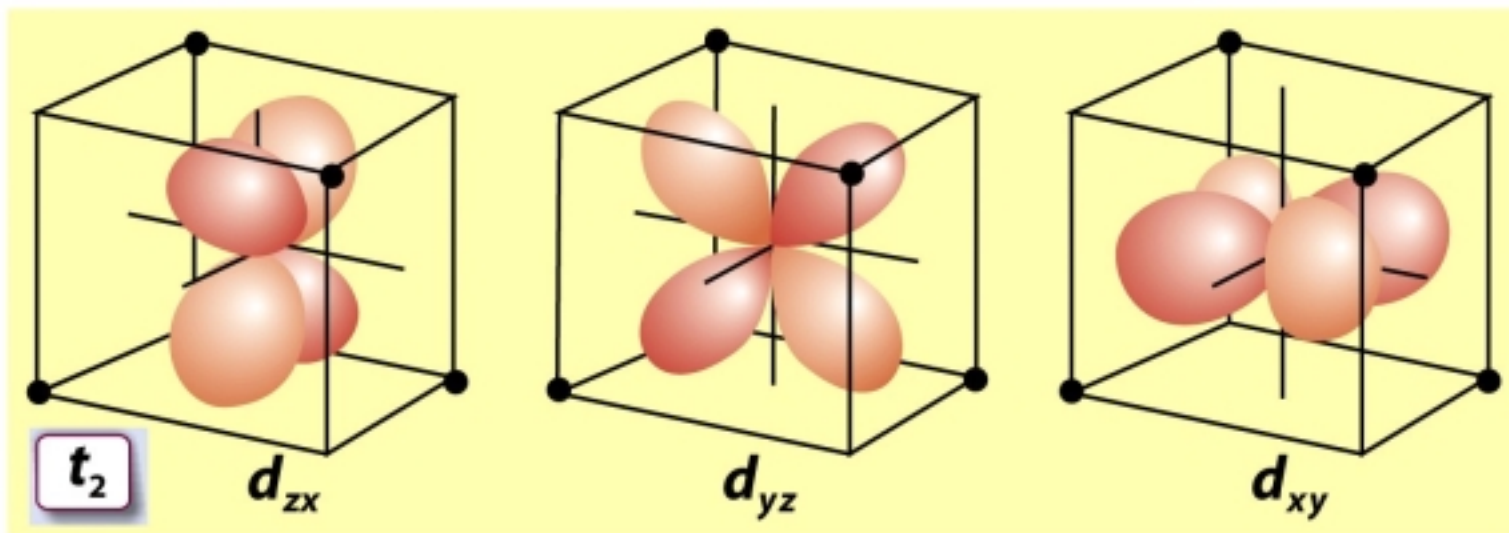
Therefore, the angle between the e-orbitals, metal and ligand is one-half of the tetrahedral angle, i.e. $109^{\circ}28' / 2 = 54^{\circ}44'$. But the angle between the t₂-orbitals, metal and ligand is one-third of the tetrahedral angle, i.e. $109^{\circ}28' / 3 = 35^{\circ}16'$.

Thus the t₂ orbitals are nearer to the direction of approach of the ligands than the e orbitals.

Hence, t₂ orbitals have higher energy compared to e-orbitals



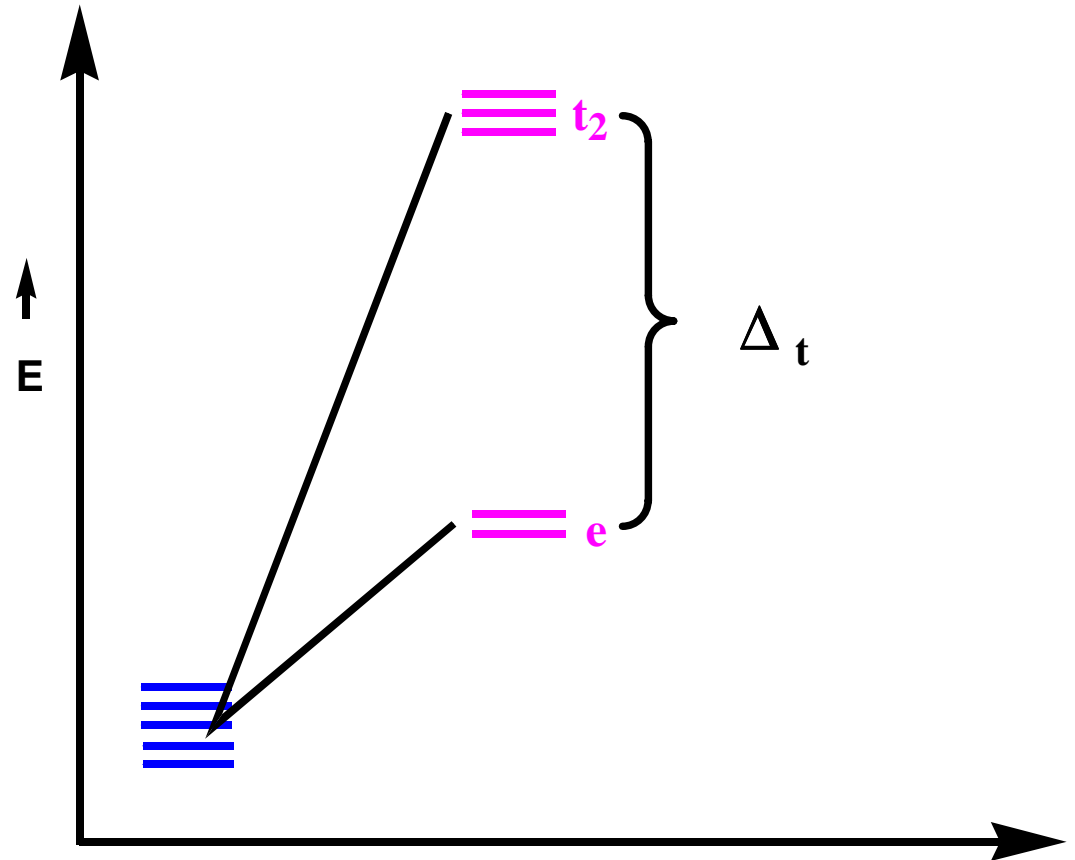
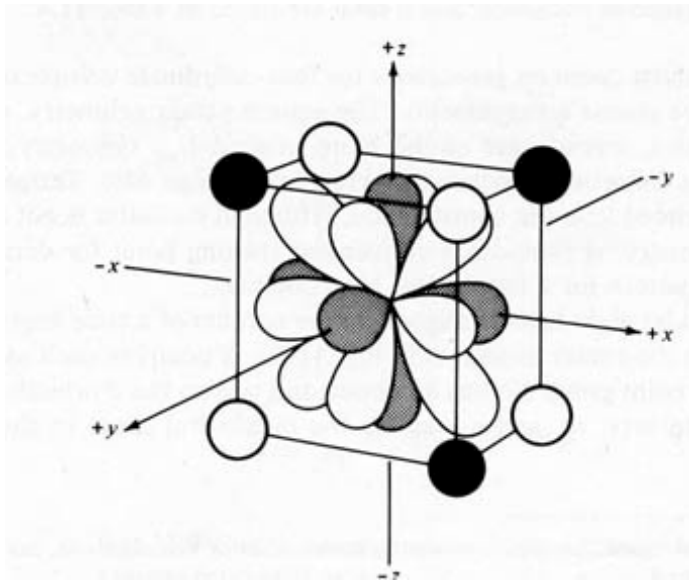
Tetrahedral Complexes



The three ' t_2 ' orbitals point to the center of the edges of the cube
 $109^\circ 28' / 3 = 35^\circ 16'$.

The two ' e ' orbitals point to the center of the face of the cube
 $109^\circ 28' / 2 = 54^\circ 44'$.

Tetrahedral Field



$$\Delta_t < \Delta_o$$

$$\Delta_t = 4/9 \Delta_o$$

There are only 4 ligands in the tetrahedral complex, and hence the ligand field is roughly 2/3 of the octahedral field.

The direction of ligand approach in tetrahedral complex does not coincide with the d-orbitals. This reduces the field by a factor of 2/3. Therefore Δ_t is roughly $2/3 \times 2/3 = 4/9$ of Δ_o .

As a result, **all tetrahedral complexes are high-spin** since the CFSE is normally smaller than the pairing energy.

Hence low spin configurations are rarely observed. Usually, if a very strong field ligand is present, the square planar geometry will be favored.

Table 19.4 Values of Δ_T for representative tetrahedral complexes

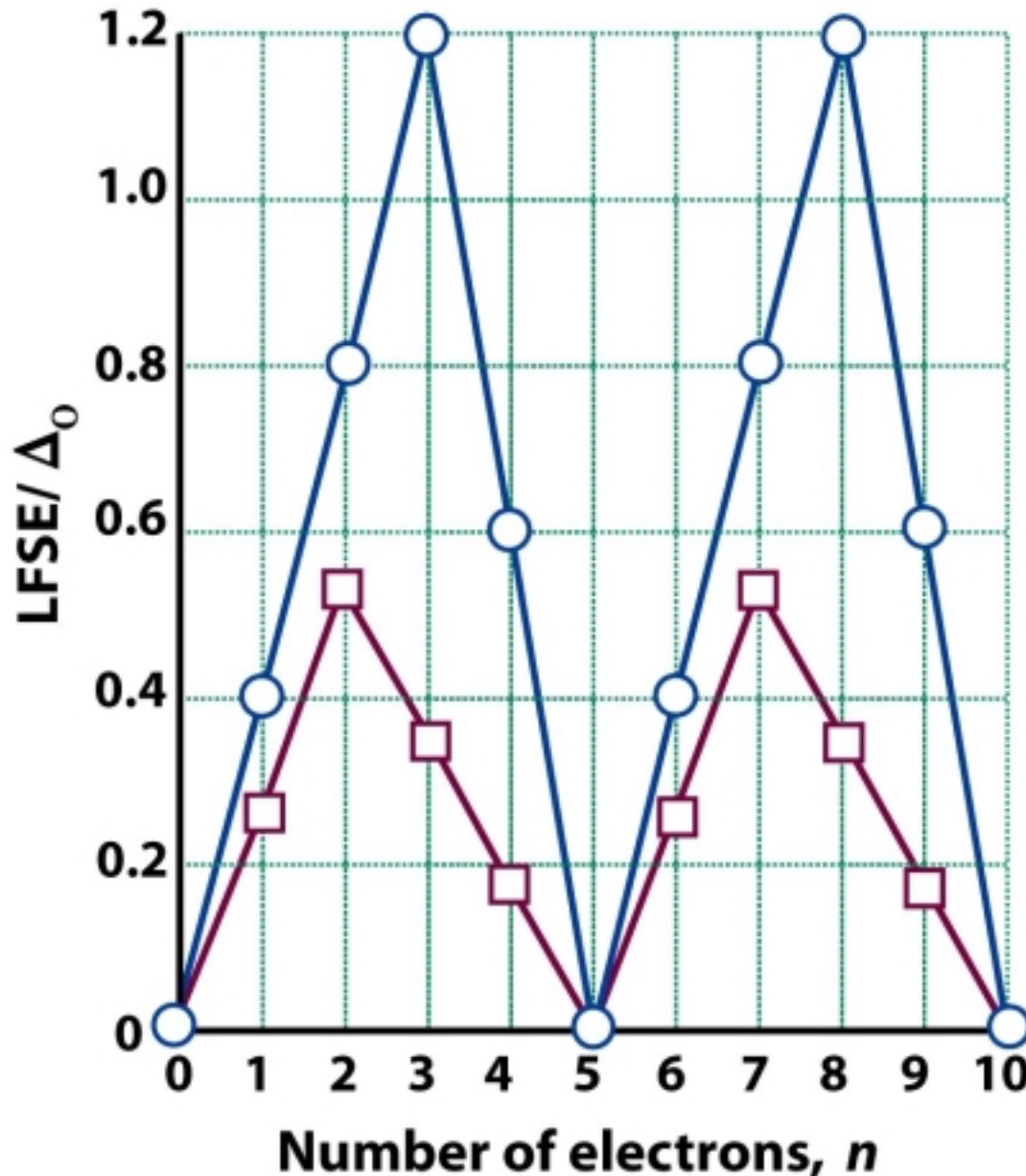
Complex	Δ_T/cm^{-1}
VCl_4	9010
$[\text{CoCl}_4]^{2-}$	3300
$[\text{CoBr}_4]^{2-}$	2900
$[\text{CoI}_4]^{2-}$	2700
$[\text{Co}(\text{NCS})_4]^{2-}$	4700

Table 19-4

Shriver & Atkins Inorganic Chemistry, Fourth Edition

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Octahedral vs. Tetrahedral Fields



Spinel - Use of CFSE

Spinel is the name given to the mineral MgAl_2O_4 .

It has a common structural arrangement shared by many oxides of the transition metals with formula AB_2O_4 .

In the **normal spinel**

The oxygens form a cubic close packed array

The Mg(II) (A-type) sit in tetrahedral sites

The Al(III) (B-type) sit in octahedral sites



An **inverse spinel** is an alternative arrangement where half of the trivalent ions swap with the divalent ions so that the Mg(II) now occupy octahedral sites ie $\text{B(AB)}\text{O}_4$.



Spinel – Use of CFSE

There are several transition metal oxides which have the formula AB_2O_4 and crystallize in spinel or inverse spinel structure. E.g. $FeCr_2O_4$, $ZnAl_2O_4$, Co_3O_4 , Mn_3O_4 , Fe_3O_4 , $NiFe_2O_4$ etc.

CFSE is highly useful to determine whether a structure would be normal or inverse

If **M^{3+} ion has a higher CFSE** in an octahedral field compared to M^{2+} ion, **normal spinel** will result.

If **M^{2+} ion has a higher CFSE** in an octahedral field compared to M^{3+} ion, **inverse spinel** will result.



Spinel - Use of CFSE

Example: Mn_3O_4

oxygen weak field ligand

Mn^{2+} ; $d^5 = t_{2g}^3 e_g^2$; no CFSE

Mn^{3+} ; $d^4 = t_{2g}^3 e_g^1$; $-0.6 \Delta_o$

Structure: **Normal Spinel**

How about Fe_3O_4 ?

Spinels - Use of CFSE

Fe_3O_4 (oxygen weak field ligand)

$\text{Fe}^{2+}; d^6 = t_{2g}^4 e_g^2; = -0.4 \Delta_o$

$\text{Fe}^{3+}; d^5 = t_{2g}^3 e_g^2; \text{no CFSE}$

Structure: Inverse Spinel

Spinel - Use of CFSE

How about MnCr_2O_4 and FeCr_2O_4 ? Work out.

Tip:

If $\text{A}^{2+} = \text{d}^6, \text{d}^7, \text{d}^8$, or d^9 ion, and $\text{B}^{3+} = \text{Fe}^{3+}$,

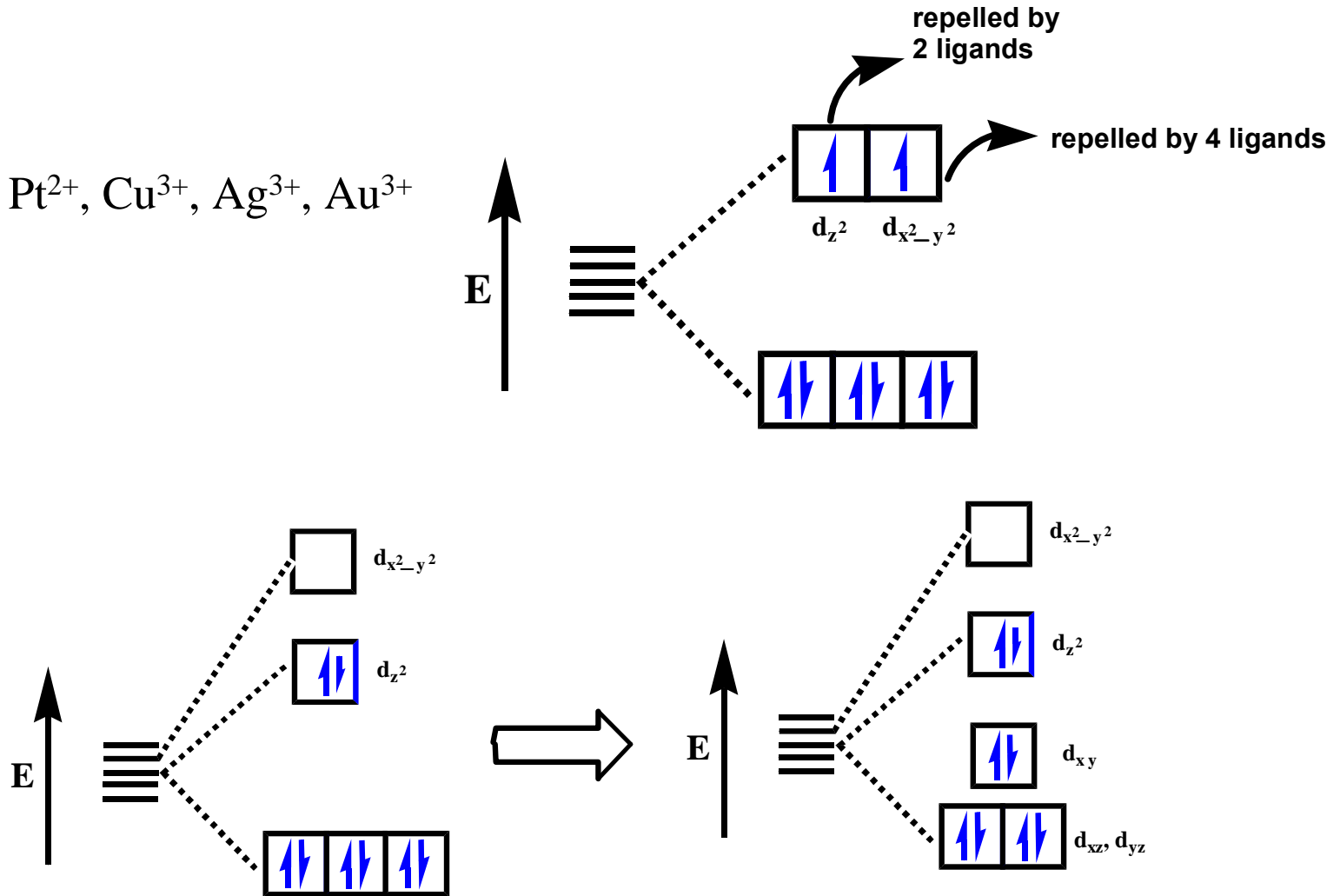
AB_2O_4 is always INVERSE.

Why ?

Special case of d⁸ Octahedral

Examples:

Ni²⁺, Pd²⁺, Pt²⁺, Cu³⁺, Ag³⁺, Au³⁺



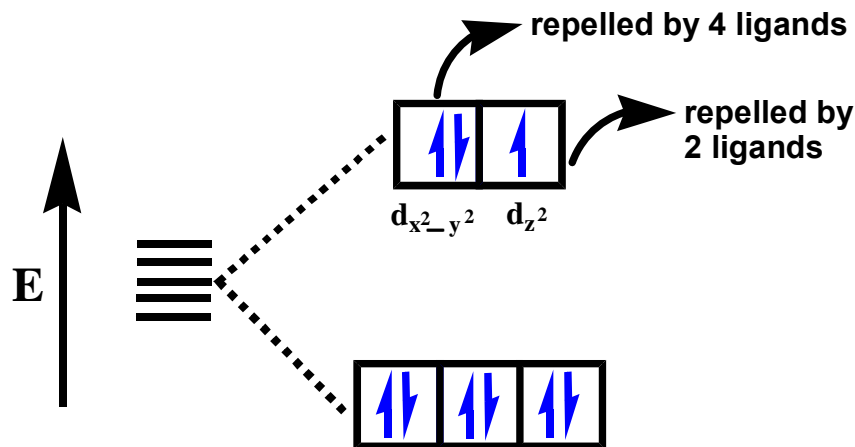
Square-planar complex is formed ; attempts to form octahedral complexes become impossible

Special case II

Jahn-Teller Distortion

If both the e_g orbitals are symmetrically filled - all ligands are repelled equally. **Result:** regular octahedron

If **asymmetrically** filled - some ligands are repelled more than the other. **Result:** Distorted octahedron



Consider e_g configuration: $(d_{z^2})^1 d_{x^2-y^2})^2$

Ligands along x , $-x$, y , $-y$ will be repelled more and bonds elongated. i.e. the octahedron will be compressed along the z axis.

Consider e_g configuration: $(d_{z^2})^2 d_{x^2-y^2})^1$

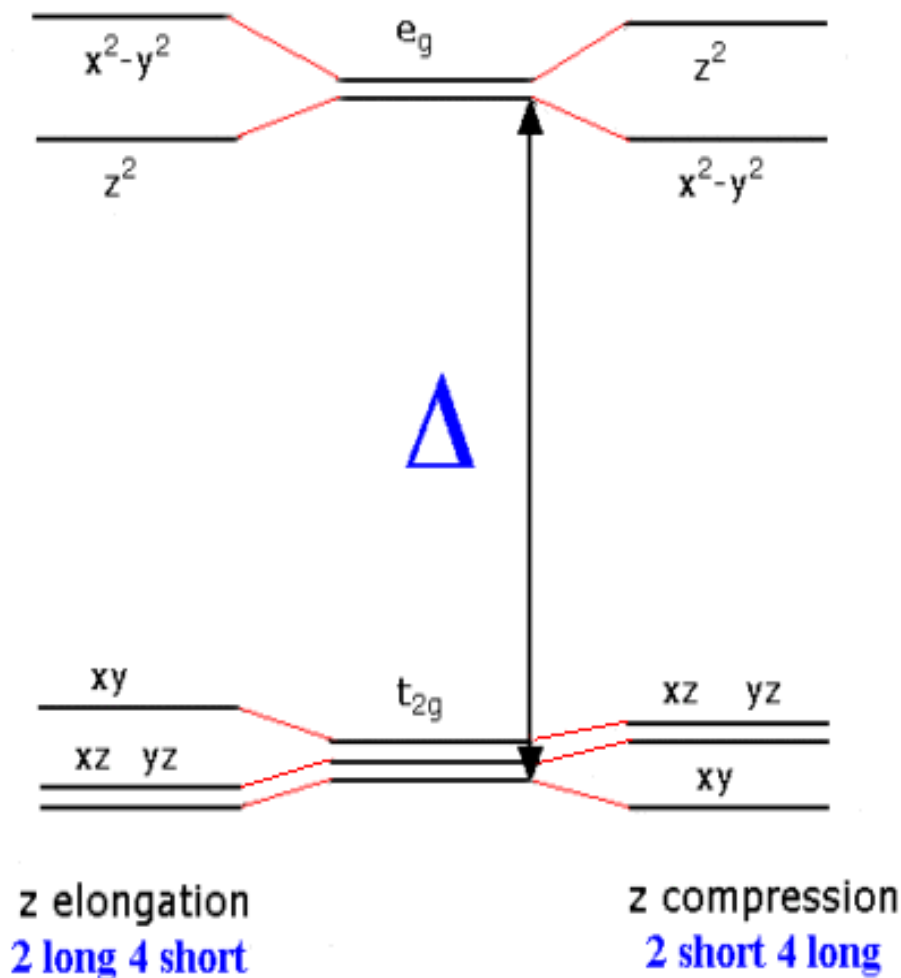
Ligands along z , $-z$ will be repelled more and bonds elongated. i.e. the octahedron will be elongated along the z axis.

The Jahn-Teller Theorem was published in 1937 and states:

"any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy thereby removing the degeneracy"

The e_g point along bond axes.

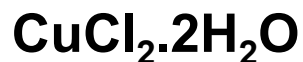
The effect of JT distortions is best documented for Cu(II) complexes (with 3e in e_g) where the result is that most complexes are found to have elongation along the z-axis.



Jahn-Teller distorted complexes



4 Br at 240pm 2 Br at 318pm



2 O at 193pm 2 Cl at 228pm 2 Cl at 295pm



4 Cl at 230pm 2 Cl at 265pm



4 F at 193pm 2 F at 227pm



4 N at 205pm 1 O at 259pm 1 O at 337pm



4 F at 191pm 2 F at 237pm



4 F at 200pm 2 F at 243pm



4 F at 214pm 2 F at 200pm



2 F at 209pm 2 F at 191pm 2 F at 179pm

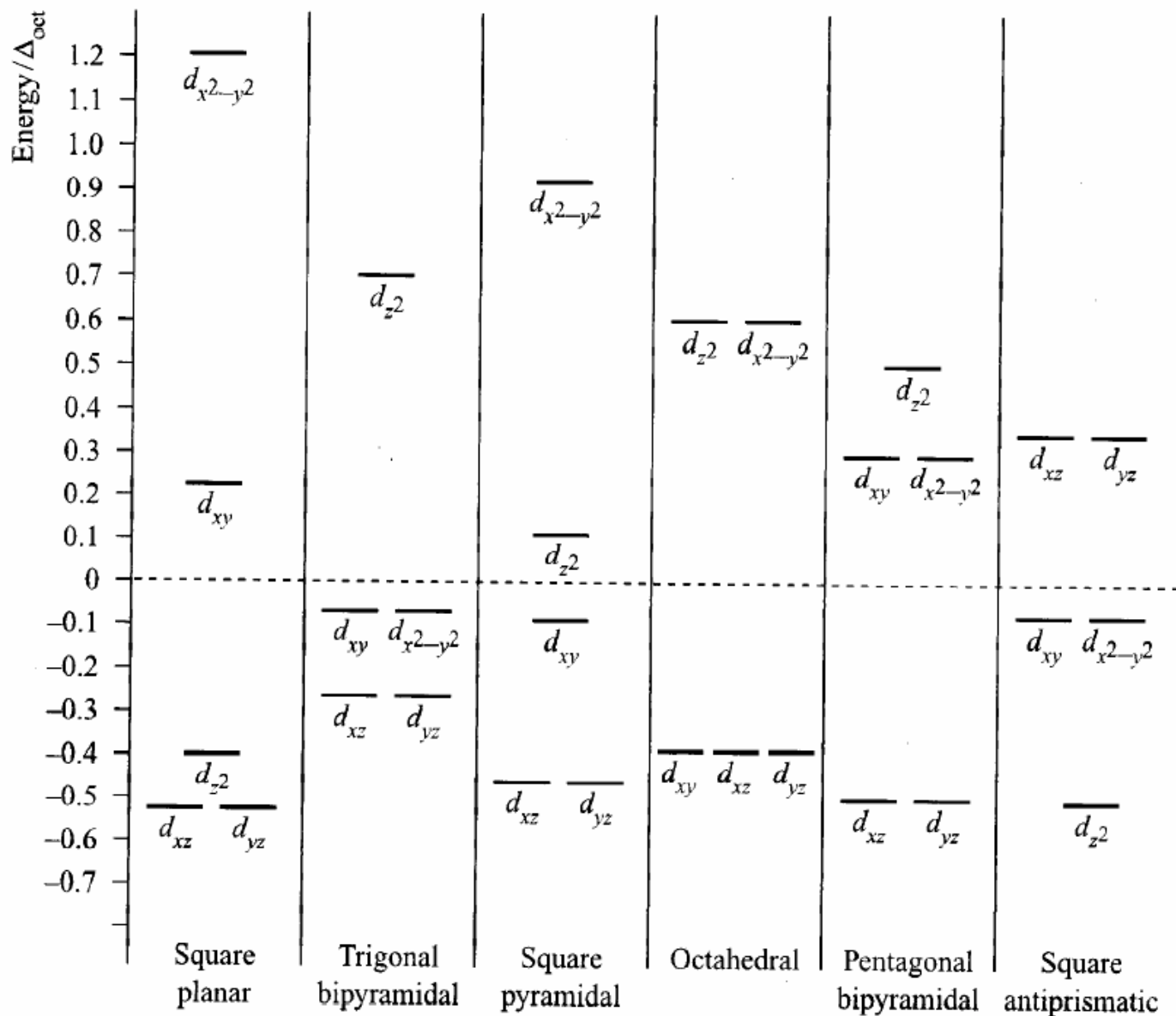


Figure 2 Crystal field splittings of d orbitals